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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

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If no title is shown please refer to the description.
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Polymer composition comprising a thermoplastic elastomer

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Polymer composition comprising a thermoplastic elastomer

The present invention relates to a polymer composition comprising a thermoplastic elastomer; to a film or tube comprising a layer including such a composition and to specific applications thereof.

Articles intended for medical applications must meet not only conventional requirements, such as good mechanical strength or low cost, but also requirements - extremely strict - peculiar to this specific field of application, such as, for example, requirements relating to the biocompatibility properties of the said articles, their ability to be subjected to a sterilization treatment, their flexibility, their transparency, their weldability, their impact strength (including
10 as regards containers filled with liquid), the amount of substances which migrates (for example in medical (fatty) liquids) or can be extracted (for example, with hexane and/or purified water) and in some cases, their barrier properties.

Until now, commercially available articles for medical use, for example
15 infusion or blood bags, and bags intended for the conservation of medical related fluids, have been based on vinyl chloride polymers, for example on PVC. Although having several advantages, this type of polymer, however, has certain disadvantages, such as the need to incorporate high amounts of stabilizers therein for the purpose of improving its thermal stability or to incorporate high amounts
20 of plasticizers therein for the purpose of obtaining sufficient flexibility. There is therefore a market demand for articles for medical applications which are devoid of chlorinated polymers.

To get such articles, it is known to start from polyolefin-based films and to weld these together (or on themselves) in order to make bags or pouches. It is
25 more specifically known to use polypropylene (PP) based films which include additives in order to improve some of the above mentioned properties. Such additives are often elastomers used to improve the transparency and flexibility of the PP resins. An example of such elastomers are those including styrene and isoprene and/or vinylisoprene units (hereafter called "SI" resins), hydrogenated
30 or not. Among those, styrene-vinylisoprene-styrene block copolymers (SVIS) and styrene-isoprene-butadiene-styrene (SIBS) are preferred because they have an improved compatibility with PP resins, especially when they are at least

partially hydrogenated. However, after a while (or after a heat treatment like heat sterilisation), it appears that films made of PP and SI resins lose their transparency, which would indicate that some phase separation appears after long term use/storage.

5 The applicant found that surprisingly, when choosing a syndiotactic polypropylene resin (s-PP), this long term phase separation tends to disappear. Another advantage of using s-PP over "conventional" i-PP is its lower melting point (130°C versus 165°C) which allows welding at lower temperature, while still allowing steam sterilisation at the classical temperature of 121°C.

10 Accordingly, the present invention relates to a polymer composition comprising a SI and a s-PP.

 The SI resin used in the composition according to the present invention is generally a triblock copolymer having two polystyrene outer blocks and a midblock including isoprene and eventually other monomers and which may be
15 partially or fully hydrogenated. The term "partially hydrogenated" means that there are still some unsaturated isoprene units left in the structure. Usually, in commercial hydrogenated SI resins, there are about 5 wt% dienes (insaturations) left or less, preferably 1 wt% or less, and most preferably, 0.5wt% or less. Fully or almost fully hydrogenated resins are preferred for stability reasons.

20 Examples of such resins are those commercialised by KURARAY under the trade name HYBRAR. These resins include till about 40% (in weight) of styrene which forms blocks linked together by blocks made of vinyl-isoprene-copolyisoprene. Grades 5127 and 5125 are non-hydrogenated while grade 7125 is hydrogenated. Hydrogenated SVIS resins like HYBRAR 7125 are preferred.

25 Other examples of such SI resins are styrene-isoprene-butadiene-styrene resins (SIBS). Examples of such resins which give good results are those commercialised under the name KRATON® G-1730, RP-6924 and RP-6917. These resins are fully or almost fully hydrogenated (i.e. they have less than 0.2 wt% of insaturations left).

30 The s-PP according to the present invention may be a homopolymer or a copolymer of propylene with up to 30% of a C₂-C₈ comonomer, preferably ethylene. It preferably is a polyolefin of controlled crystallinity as described in WO 00/61062. It preferably shows a softening point (or "Vicat Point") of less than 121°C (measured according to ASTM Standard D1525), at least after
35 having been processed in appropriate conditions (which are described in WO 00/061062, incorporated herein by reference), even if the producer of the resin

announces higher values. The s-PP according to the present invention thus preferably exhibit the distinguishing feature that their crystallinity can be easily reduced during their processing. This ready control of the crystallinity is advantageous in the content of the invention, in so far as it makes it possible to confer a reduced crystallinity on these s-PP resins, provided that appropriate processing conditions are used, thus increasing the transparency and the flexibility of the whole structure.

The polydispersity of the s-PP according to the present invention is advantageously less than 8 and preferably less than 4. This characteristic reflects a low dispersion of the molecular masses, which increases the separation between the melting temperature ranges and softening temperature ranges and thus makes it possible to have a more effective action on the crystallinity during the processing.

Furthermore, the melt flow index of the s-PP used is advantageously less than 12 g/10 min, preferably less than 10 g/10 min and most preferably less than 8 g/10 min (measured according to ASTM Standard D1238, under the conditions 190°C/2.16 kg for the polymers of ethylene and the copolymers of butene and under the conditions 230°C/2.16 kg for the polymers of propylene and the homopolymers of butene).

In the composition according to the present invention, the s-PP is generally present in an amount of 30% or more, or even 40% or more (in weight compared with the total weight of the blend). On the other hand, the SVIS content of the blend is generally of 5% or more, or even 10% or more. Generally, the s-PP is present in amount of 95% or less, or even 90% or less, while on the other hand, the SVIS is generally present in amount of 70% or less, or even 60% or less.

The composition according to the present invention may include other polymers and/or usual additives like pigments, stabilizers ... Especially when it is intended to be welded, it may comprise at least one not very crystalline or amorphous polyolefin chosen between ethylene-vinyl acetate (EVA), ethylene-methyl acrylate (EMA), ethylene-ethyl acrylate (EEA) or ethylene-butyl acrylate (EBA) copolymers. Among the last mentioned copolymers, only those which exhibit a content of comonomer(s) of at least 9% naturally come into consideration as additional constituents. The concentration of these copolymers is generally equal to or higher than 0.05% (in weight with relation to the entire composition), and preferably higher than 0.1%. It is generally equal to or lower than 15%, preferably than 10% and most preferably than 5%. A mixture of EVA

an EMA, preferably in a total amount of at least 0.1%, or even at least 1%, but not exceeding 5%, gives good results. It makes it namely possible to make welds with very reproducible peel strengths, which is very useful for making items with a peelable seal, like multi-chamber bags or pouches including a permanent, outer seal and at least one peelable seal.

The composition according to the present invention may easily be processed in any kind of object, from a flat one (like a film or sheet) to a three dimensional one (like a container or a tube), and either into a monolayer structure or into a multilayer one.

Preferably, the present invention relates to a film or a tube comprising at least one layer including the above described composition.

The term "film" is used to denote a thin, flat structure (in the case of cast films for instance) or a tubular one (in the case of blown films for instance) which generally has a thickness of 1000 μm or less, preferably 500 μm or less, or even 250 μm or less. In practice, a thickness of 90 μm or more is suitable, or even 140 μm or more. The term "tube" is used to denote a tubular structure which generally has a wall-thickness of 200 μm or more, preferably 500 μm or more. In practice, this thickness is often lower than 2500 μm . Such tubes can serve as a port member for a medical packaging unit (like for instance a container, pouch, bag and the like).

Preferably, the composition described above is used in a multilayer structure (film or tube) which includes several layers providing specific properties like barrier properties, sealability etc. In a preferred embodiment, the composition is included in the sealing layer of the structure (film or tube). By "sealing layer" is meant a layer which actually melts during welding (either permanent or peelable seals), which is usually a surface layer and has in general the lowest melting point of the structure. It is namely so that the SI resin (as being a thermoplastic elastomer with glass transition temperatures below 0°C) is soft at ambient temperatures or above and that the s-PP has a rather low melting point so that their mixture shows excellent sealability. In this embodiment, as already explained above, the sealing layer preferably comprises additionally EVA and/or EMA, in the amounts specified above, but preferably equal to or less than 5% in weight in order not to lose transparency.

Multilayer structures (like films or tubes) according to the present invention may include at least one barrier layer comprising resins like EVOH, PA, polyester, LCP (liquid crystal polymer), ... or their mixtures. In a preferred

embodiment, pure EVOH is used as barrier resin, more particularly an EVOH with an ethylene content in the range between 20 and 45 mol%, preferably between 25 and 40 mol% and most preferably around 30 mol% this to withstand steam sterilization at 121°C/250 °F. A suitable commercial grade of EVOH is

5 Kuraray EVAL™ 101B (27 mol% ethylene). In another preferred embodiment, EVOH is mixed/blended with polyamide (PA) to improve barrier properties at higher humidity. Examples of such PA resins are PA11 or PA12 (for instance Rilsan® B or Rilsan® A from Atofina), PA6/66 (for instance Capron® CF120 ZI from BASF) or FDA 21 CFR 177.1500 and EU directive 2007/72/EC compliant

10 PA6 (like for instance Capron® from BASF, Durethan® T40 from Bayer) or PA 6/12 (Zytel® from Dupont). The ones which have a melting point (measured by DSC {endotherm peak temperature}) around 200°C are preferred. The ones having a Vicat softening temperature (ISO306 50N;120°C/h) below 150°C are preferred as well to gain some flexibility. Yet in another preferred embodiment, a

15 layer of EVOH is combined with at least one layer of a suitable PA (PA11, 12, 6, 6/66, 612 and the like) as mentioned above in order to get maximum transparency in combination with high barrier properties. For medium barrier films a layer of a suitable PA (PA11, 12, 6, 6/66, 612 and the like) may be included.

20 To adhere polyolefin containing layers to such barrier layers, tie layers like for instance maleated thermoplasts (Bynel® from Dupont, Admer® from Mitsui, Orevac® from Atofina, Priex® from Solvay, ...) and/or thermoplastic elastomers (Kraton® FG 1901, FG 1921, FG 1924) are used. Of particular interest is a maleated s-PP eventually blended/mixed with a maleated thermoplastic

25 elastomer.

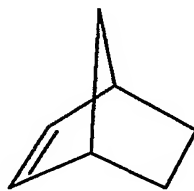
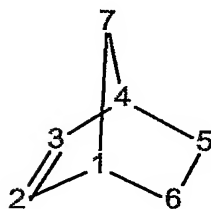
According to one embodiment, the film includes as barrier layer, a layer including a cyclic olefin resin (COP) which may be a thermoplastic or an elastomer, or a mixture of both. This allows to get better barrier properties against the migration of alcohols, acids and water (or vapour).

30 The term "COP" is understood to mean a homo- or a copolymer of a C₅ to C₁₂ cyclic monomer and/or di-cyclic monomer (dimer), which may bear side chains so as to reach a total of 5 to 30 C. Cycloolefin copolymers in general consist besides the cyclic monomer of a C₂ to C₁₀ olefin monomer. They are in general amorphous or semi cristallin plastics whose softening points and glass

35 transition temperatures (T_g) can be adjusted over a wide temperature range by varying the proportion of comonomer. Those having a cyclic monomer content above approximately 20 wt% are relatively brittle and have a T_g above room

temperature. Those having a cyclic olefin content below approximately 20 wt% are having a Tg below room temperature and are therefore elastomeric in nature (having an elongation at break of at least 50%). Of particular interest are those having a cyclic olefin content of at least 40 wt%, preferably of 50 wt% or more and most preferably those having a cyclic olefin content of 60 wt% or more and those having a cyclic olefin content of 20 wt% or less or 2% or more. Of particular interest are the ones with a Tg of 121°C or more while they are steam sterilisable and the ones having a cyclic olefin content of less than 20 wt% while they show some cristallinity and thus having a melting point, which is advantageous for sealing and other heat treatments. The applicant found that surprisingly, when mixing a COP with a high Tg and one with a low Tg, certain properties in terms of flexibility, transparency, sterilisability and sealability, which are most wanted in the art for medical applications could be combined.

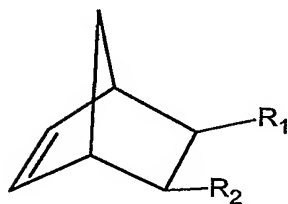
The basic cyclic monomer unit can be cyclopentene, cyclohexene, norbornene, dicyclopentadiene, tetracyclododecene or methyltetracyclododecene. It is preferably norbornene :



bicyclo[2.2.1]hept-2-ene

eventually bearing side chains which may be linear :

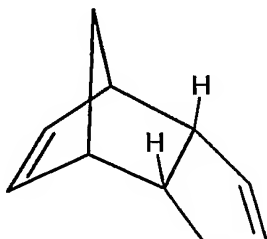
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bicyclo[2.2.1]hept-2-ene

R1, R2 ($=C_xH_{y+1}$ with $x, y = 0, 1, 2, \dots$)

or cyclic, like in dicyclopentadiene (which is in fact norbornene with a cyclopentadiene side chain) :



- 5 The olefin is advantageously ethylene. The COP is preferably a homo- or copolymer of norbornene with or without side chains; it is more preferably either a homopolymer of norbornene (with or without side chains, but preferably with cyclopentadiene as side chain, i.e. it is preferably a homopolymer of dicyclopentadiene), or a copolymer of norbornene (with or without side chains) and ethylene. In the latter case, the content of ethylene is advantageously between 80 and 98 wt% or below 60 wt%.

According to this embodiment, the COP may be blended with another polymer or with a hydrogenated hydrocarbon. Advantageously, the COP is blended with s-PP in order to make the film/tube more tough and ductile and impact and puncture resistant, easy to weld and to steam sterilise, but other thermoplastic polymers/elastomers and hydrocarbons may be used as well to dilute/ blend the COP. These are advantageously chosen from not very crystalline or amorphous polyolefins or hydrocarbons like the SI resins described above or those of the following types :

- 20 – olefinic copolymers composed of at least two C_2 to C_{10} alkenes, comprising at least 60% by weight of ethylene and/or of propylene and/or of butene but not comprising more than 90% by weight of the same comonomer, or from
- olefinic copolymers comprising ethylene and/or propylene and/or butene and from 10 to 40% by weight of one or more different comonomers which are preferably chosen from C_5 to C_{10} olefins [for instance copolymers of ethylene and 1-octene in an amount such to have linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) or ultra low density polyethylene (ULDPE)] and carboxylic acid or ester groups, for example vinyl acetate, methyl, ethyl or butyl acrylate and methyl methacrylate, or
- 30 carbon monoxide, or from

- elastomeric copolymers or terpolymers with blocks of styrene and of one or more olefins (for example, copolymers of the styrene-butadiene-styrene (SBS), styrene-ethylene-butylene-styrene (SEBS) or styrene-ethylene-propylene-styrene type (SEPS), and the like), or from
- 5 – highly branched homopolymers [for example, low density polyethylene (LDPE) or medium density polyethylene (MDPE)] or from
- hydrogenated hydrocarbons like paraffin or paraffinic oil.

Advantageously, the COP comprising layer comprises at least one resin chosen between SI resins, styrene-ethylene-butylene-styrene (SEBS), eventually
10 including styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), eventually including styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers (preferably made by metallocene technology). SI resins, SEBS and/or SEPS are preferred because they allow to make both permanent
15 seals and peelable seals (at a lower temperature) and because they improve its impact strength. The total concentration of these resins is generally equal to or higher than 1% (in weight with relation to the entire layer composition), and preferably equal to or higher than 5%. It is generally equal to or lower than 39%, preferably than 30%.

Since COP resins are sensitive to grease, even in low amounts such as
20 when touching or manipulating it, the COP comprising layer according to this preferred embodiment of the present invention is advantageously an internal layer, comprised in between two other layers. One of these layers may be the SI and s-PP comprising layer.

The films/tubes according to the present invention may also include a
25 high melt temperature ($>130^{\circ}\text{C}$), flexible, transparent outer layer (i.e. a layer on the outside of the structure, on the other side of the sealing layer). This layer may comprise a thermoplastic polyester elastomer (TPE) and/or PEBA (polyester block amide copolymers). TPE resins are composed of alternating hard poly-1,4-butanediol and/or poly(alkylene oxide)glycol, terephthalate acid or 1,4-
30 cyclohexane-dicarboxylate and 1,4-cyclohexane-dimethanol block copolymers connected by ether and ester linkages. Examples of such TPEs are ECDEL[®] resins (PCCE or polycyclohexane dicarboxylic acid – cyclohexane dimethanol – elastomer or copolyester based on 1,4-cyclohexanedicarboxylic acid, 1,4-cyclohexanedimethanol, and poly (oxytetramethylene) glycol) commercialised
35 by Eastman, HYTREL[®] resins from Dupont, LOMOD[®] resins from GE and RITEFLEX[®] resins from Celanese. PEBA resins are composed of polyamide

blocks and at least a block of poly(alkylene oxide). Such resins are for example commercialized by Atofina chemicals PEBAX®.

The above mentioned outer layer of the film according to the present invention may also comprise an SI or SEBS, SBS, ... resin (i.e. block
5 copolymers having outer blocks of styrene and a midblock comprising at least one polyolefin or isoprene, as described above) to reduce sticking of the film to itself when stored (folded or rolled up) and/or to its packaging.

Besides the sealing layer, barrier layer and outer layers mentioned above, the films/tubes according to the invention may include at least one additional
10 internal layer, with a melting point in between those of the sealing and outer layers and including similar polymers (chosen between one or more of SI resins, s-PP, other PP resins, elastomers, ...). For instance, it may be of interest from an economical point of view to include a layer made of scraps (i.e. production waste of films/tubes according to the present invention), as internal layer in the
15 films/tubes described above. Whatever the number of layers, it is generally interesting to have a melting point gradient in the structure, in which the layer with the lowest melting point being the sealing layer.

According to an embodiment of the present invention, the multilayer structure (film or tube) described above comprises a more than 40% in weight of
20 metallocene technology PO resins from which at least 30 wt% PP resins (either syndiotactic or isotactic, either homo- or copolymer, for instance with ethylene). The choice of PO resins obtained through metallocene catalyst technology improves the purity (content of extractibles and catalytic residues) of the entire structure. These metallocene PP resins are preferably s-PP and/or i-PP.

25 Films according to the present invention may be fully or partially (partially meaning with a window) embossed (i.e. may carry a pattern in relief) by any known technique in order to prevent blocking.

Films according to the present invention are very easy to weld and can therefore very conveniently be used to make bags. Accordingly, the present
30 invention also relates to a bag made by welding a film as described above. Preferably, this bag is a multi-chamber bag including at least one permanent, outer seal and at least one peelable seal. By permanent seal is meant a seal which cannot be peeled easily manually and which generally shows a peel strength of at least 2000 N/m (according to ASTM/ISO F88), or even at least 3000 N/m, while
35 a peelable seal is a seal easy to peel manually and which generally shows a peel strength of less than 2000 N/m. The optimal temperature, pressure and welding time ranges to respectively get a permanent and a peelable seal with a given

structure can very easily be determined by one of ordinary skill in the art, using a few experiments. Generally, permanent and peelable seals are made using hot gas or hot tool welding, the latter being preferred.

5 The films, tubes and bags according to the present invention may be used for any application where their above mentioned properties are valuable. The medical field is such an application area. Bags according to the present invention are indeed particularly suitable for containing medical fluids like dialysis, infusion, nutrition, ... solutions.

10 Finally, the polymer composition according to the present invention can also advantageously be used in injection moulded articles. It is namely so that in most application area of the above mentioned film and bag, the latter have to be connected to some kind of apparatus (like a perfusion or dialysis apparatus for instance) and to perform this connection, often connecting parts are used, which are generally made by injection moulding. In order to have a complete system of
15 the same polymer ingredients, and to benefit of the advantages thereof as set forth above, these injection moulded articles advantageously include the same polymer composition as the one described above.

CLAIMS

- 1 - Polymer composition comprising a thermoplastic elastomer including styrene and isoprene and/or vinylisoprene units (SI) and a syndiotactic polypropylene (s-PP).
- 5 2 - Polymer composition according to claim 1, in which the SI is at least partially hydrogenated.
- 3 - Multilayer structure at least one layer including a polymer composition according to claim 1 or 2.
- 10 4 - Multilayer structure to the preceding claim, which is a multilayer film or tube and in which the layer including the polymer composition according to claim 1 or 2 is the sealing layer.
- 5 - Film or tube according to the preceding claim, in which the sealing layer comprises additionally EVA and/or EMA.
- 15 6 - Film or tube according to any of claims 4 or 5, having at least one barrier layer comprising resins like EVOH (ethylene vinyl alcohol copolymer), PA (polyamide), polyester, LCP (liquid crystal polymer) or mixtures thereof, or a cyclic olefin polymer (COP).
- 20 7 - Film or tube according to any of claims 4 to 6, having an outer layer comprising a thermoplastic polyester elastomer (TPE) and/or a PEBA (polyester block polyamide).
- 8 - Film or tube according to any of claims 4 to 7, which comprises a major more than 40% in weight of metallocene technology PO (polyolefin) resins from which at least 30 wt % PP (polypropylene) resins.
- 9 - Bag made by welding a film according to any of claims 3 to 8.
- 25 10 - Injection moulded article comprising a polymer composition according to any of claims 1 or 2.

ABSTRACT

Polymer composition comprising a thermoplastic elastomer

Polymer composition comprising a thermoplastic elastomer including styrene and isoprene and/or vinylisoprene units (SI) and a syndiotactic polypropylene (s-PP).

No figure.

